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CHANGES IN OXIDIZING POTENTIAL OF GLASS MELT UPON REPLACING RAW MATERIALS IN PRODUCTION OF PHOTOCHROMIC GLASS

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Variations in the redox potential of glass melt in production of photochromic glasses in the case of partial of total replacement of soda ash and alumina by natural aluminosilicate materials are considered.

Photochromic glasses (PCG) reversibly change their light transmission under the effect of sunlight and therefore are widely used to protect eyesight and to develop light filters with modulated light transmission. Such glasses are traditionally produced in the $Na_2O – Al_2O_3 – B_2O_3 – SiO_2$ system complicated by light-sensitive and technological additives (Cu_2O, CdO, NaCl, SnO, Na_2SiF_6). Batches are prepared from synthesized materials, which makes PCG very expensive and restricts their applications areas [1]. One of the ways to lower the cost of such glasses is using natural materials in their production. However, this problem is not sufficiently studied and the data published in the literature are contradictory.

The purpose of the present study is to identify the range of PCG compositions in which natural aluminosilicate materials can be used.

Glasses of the $Na_2O – Al_2O_3 – B_2O_3 – SiO_2$ system complicated by additives of Cu_2O, CdO, NaCl, SnO, and N_2SiF_6 were investigated. The glasses were synthesized using artificial materials (H_3BO_3, Na_2CO_3, Al_2O_3, SiO_2, $Na_2B_4O_7 \cdot 10H_2O$) and natural silicates and aluminosilicates [quartz sand, concentrated feldspar and pegmatite, alkaline and low-alkali kaolins (Table 1)]. The traditional methods of synthesis and analysis of glass properties were used [2].

The above-mentioned natural materials introduce basic (SiO_2, Al_2O_3, Na_2O) and impurity (CaO, MgO, K_2O, TiO_2, Fe_2O_3) oxides into PCG compositions. It is demonstrated in [3] that CaO, MgO, and TiO_2 do not adversely influence the photochromic effect. Potassium and iron oxides behave in a slightly different way. The former has a clearly alkaline nature with a perceptible effect on the redox potential of glass (ROP), and the latter is the oxide of a variable-valence element that exists in the glass melt both in the form of Fe(II) and Fe(III), and the state of equilibrium between these two forms to a large extent depends on the ROP of glass. It is known that iron and copper in glass melt mutually affect each other [4], and we believe that this will affect the photochromic properties of glass depending on the concentration of light-sensitive CuCl crystals.

Consequently, for successful use of natural materials in the PCG technology, two problems have to be solved:

– estimating changes in the ROP of glass after the introduction of natural aluminosilicates;

– controlling the modification of the glass ROP to achieve the required level of photochromic properties.

A qualitative evaluation of changes in the ROP of glasses with variable light transmission upon using feldspar concentrate (FC) in its synthesis was performed for high-alkali glasses of series D with the following molar composition: $13.4Me_2O \cdot 6.6Al_2O_3 \cdot 20B_2O_3 \cdot 60SiO_2$. The weight content of FC in mixture compositions was consecutively increased from 0.01 to 0.13% and that of alkaline-earth metals and potassium from 0.00 to 0.36 and to 2.67%, respectively.

TABLE 1

Material	Mass content, % (based on analysis)						
	SiO_2	Al_2O_3	Na_2O	K_2O	MeO	Fe_2O_3 + TiO_2	calcination loss
Quartz sand	99.83	0.10	–	–	0.02	0.05	–
Concentrate:							
pegmatite	74.72	13.97	4.40	3.80	1.18	0.67	1.26
feldspar	68.78	21.04	7.85	5.32	0.80	0.30	–
Kaolin:							
low-alkali	47.86	36.26	0.69		0.66	2.65	12.31
alkaline	44.37	30.08	13.14	7.00	1.28	2.83	1.30

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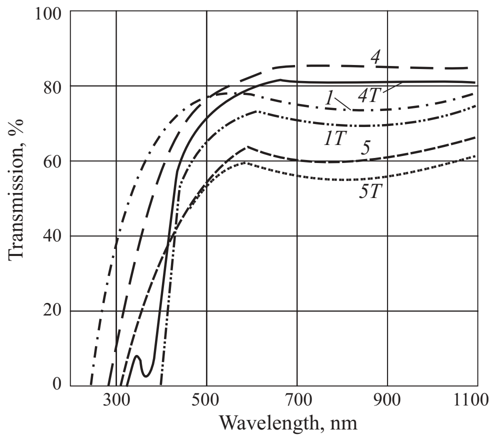

Fig. 1. Transmission spectra of PCG of series D (sample thickness 0.87 mm): *1* and *1T*) without FC in the batch; *4* and *4T*) 22.0% FC; *5* and *5T*) 31.0% FC; *1*, *4*, and *5*) after annealing; *1T*, *4T*, and *5T*) after additional thermal treatment.

As the method of joint identification of variable-valence elements in PCG is absent, the following assumptions were made.

– a high rate of viscosity increment in glass melt cooling determines an invariable redox equilibrium of the variable-valence elements in their transition from melted to solid glass;

– formation and growth of light-sensitive CuCl microcrystals occurs during additional heat treatment of samples.

These assumptions make it possible to study separately the changes in the redox equilibrium (on samples after annealing) and the emergence of light-sensitive CuCl crystals (on glasses after additional heat treatment).

Figure 1 shows the absorption spectra of series D glasses measured after annealing (with a SF-20 instrument). The glass synthesized from pure chemicals (curves *1*) contains 0.01% Fe_2O_3. Spectral curves *4* and *5* are obtained after studying glasses whose batches contain 22.0 and 31.0% FC respectively (0.08 and 0.12% Fe_2O_3). The glass synthesized without FC exhibits high light transmission in the UV and visible spectrum ranges, as well as the presence of copper in its highest valence state (Cu^{2+}) (wide absorption band with maximum at a wavelength of 790 nm). The introduction of FC increases the concentration of bivalent copper (curve *5*, intensified absorption at a wavelength of 790 nm). The simultaneous shift of the absorption band edge from 360 to 450 nm indicates an increased content of iron in the oxidized form (Fe^{3+}) in glass 5. The content of reduced iron (Fe^{2+}) in this case does not vary. The considered glasses have no photochromic properties after annealing.

Additional heat treatment of glass samples changes the course of the spectral curves. The shift of the absorption band edge in spectral curves *1T* and *4T* by 80 and 50 nm, respectively, compared with curves *1* and *4*, and the emergence of a peak with the absorption maximum at 380 nm in glass *4T* point to the formation of the light-sensitive phase CuCl in the glass. Its concentration in glasses with FC is significantly lower than in the initial composition, which is indicated by decreased light transmission after 2.5 min of UV radiation. It is observed that within an Fe_2O_3 content interval equal to 0.01 – 0.06% the photochromic properties of glasses based on FC vary insignificantly. A further increase in the content of Fe_2O_3 produces a sharp deterioration of the photochromic properties, as the consequences of the redox equilibrium of Cu(I) shifting toward a higher content of its oxidized form (Cu^{2+}) and increased absorption in the UV spectrum range of glasses with Fe_2O_3.

All this is evidence of a high initial ROP of glass synthesized from pure chemical reactants and its subsequent growth as a consequence of partial replacement of soda and alumina in the batch by FC.

Based on the obtained results, an attempt was made to decrease the ROP of glass with an elevated content of Fe_2O_3 by modifying its basicity. For the quantitative estimate of the ROP of glasses in the $Na_2O – Al_2O_3 – B_2O_3 – SiO_2$ system, the following equation was used [5]:

$$K_{\text{bas}} = \frac{4.6x_1 - 4.7(x_2 - x_1)}{0.82x_3 + [x_4 + (x_2 - x_1)]},$$

where K_{bas} is the basicity index of glass; x_1, x_2, x_3, and x_4 are the molar contents of aluminum, sodium, silicon, and boron oxides, respectively, %.

The numerator shows the concentrations of structural groups of alkaline (base) nature, namely, $[AlO_4/2]Na$ and

TABLE 2

Glass	Weight content, %				Position of absorption band edge, nm, after		Transmission variation after UV activation, %	Glass tint
	FC in batch	impurities			annealing	thermal treatment		
		K_2O	MeO	Fe_2O_3				
1	0.0	0.00	0.00	0.01	360	440	31.5	Light green
2	4.0	0.30	0.04	0.02	–	–	28.0	Clear
3	18.0	1.23	0.18	0.06	–	–	32.0	Light yellow
4	22.0	1.39	0.23	0.08	380	430	22.0	The same
5	31.0	2.17	0.32	0.12	450	450	0.6	Yellow
6	35.0	2.67	0.36	0.13	–	–	0.6	The same

$[BO_4/2]Na$, respectively, compared to the groups of $SiO_4/2$ and $BO_3/2$. The content of the latter groups is indicated in the denominator.

The calculation carried out using the above equation yields a basicity index equal to 0.99 for the glass synthesized from chemical reactants, which correlates with the high oxidizing potential of PCG glass [5].

Decreasing the ROP of glasses by modifying the concentration of alkaline and acid oxides made it possible to identify the range of PCG which can be synthesized using natural aluminosilicates with different contents of Fe_2O_3 (Table 3).

Note that complete replacement of soda and alumina in PCG batch by mineral materials is possible provided that the following condition is satisfied:

$$[Me_2O]_{cal}/[Al_2O_3]_{cal} = [Me_2O]_{nat}/[Al_2O_3]_{nat},$$

where $[Me_2O]_{cal}$, $[Al_2O_3]_{cal}$, $[Me_2O]_{nat}$, and $[Al_2O_3]_{nat}$ is the mass content of alkaline metal oxides and aluminum oxides (calculated) in glass (cal) and in natural materials (nat), %, respectively.

If this condition is not satisfied, the PCG batch has to be corrected by additional introduction of the missing components via the respective chemical reactants.

Glasses synthesized on the basis of FC occupy the widest range of the compositions with photochromic properties (Table 3). It includes compositions containing up to 0.15% Fe_2O_3 with the estimated basicity index $K_{bas} = 0.11 - 0.45$. The FC content in the batch of these PCG reached 35.7%. Glasses within this range have stable high photochromic parameters. Their samples are tinted in various shades of yellow, the color intensity growing with increasing Fe_2O_3 content in the glass and increasing K_{bas}. When the value of K_{bas} goes beyond the upper limit ($K_{bas} = 0.45$), the reproducibility of photochromic properties deteriorates.

A similar situation was observed in glasses synthesized from batches based on pegmatite concentrate and alkaline and low-alkali nepheline. An increase in the basicity of glass and a higher content of natural materials in the batch sharply narrow the range of glasses having photochromic properties. With batches containing up to 33.0% pegmatite (iron content in the glasses up to 0.25%), photochromic properties were observed in glasses with $K_{bas} = 0.11 - 0.25$. In using alkaline and low-alkali kaolin (aluminosilicate content in batch 6 – 7%, content of Fe_2O_3 in glass 0.33 and 0.15%, respectively), the photochromic effect was registered in the compositions with $K_{bas} = 0.11 - 0.19$ (low-alkali kaolin) and 0.11 – 0.13 (high-alkali kaolin).

Thus, the deterioration of photochromic properties caused by a replacement of synthetic materials by natural aluminosilicates is due to the increased content of impurity oxides (Fe_2O_3, K_2O) in mixtures. This leads to a spontaneous increase in the oxidizing potential of glass. A modification of the latter by correcting the ratio between acid and base oxides makes it possible to obtain the photochromic effect in glasses with a high degree of acidity ($K_{bas} = 0.11 - 0.45$) containing up to 0.15% Fe_2O_3. This technique makes it possible to totally or partly eliminate soda and alumina from PCG batches and to replace them by various types of natural minerals.

An increased concentration of impurity oxides introduced with the specified materials narrows the range of PCG and shifts its upper limit toward mixtures with a high degree of acidity ($K_{bas} = 0.11 - 0.20$).

The requirements formulated with respect to aluminosilicate materials of mineral origin can be used in PCG technology. This can be any natural aluminosilicate with a constant chemical (permissible fluctuation of the basic components not more than 1%) and granulometric (0.2 – 0.3 mm frac-

TABLE 3

Material and its part (%) in the batch	PCG with weight content, %			Basicity index	Glass tint	Existence of photochromic properties
	B_2O_3	$Me_2O + MeO$	Fe_2O_3			
Feldspar concentrate:						
11.50	22.23	2.04	0.07	0.11	Light yellow	Present
24.50	16.50	4.46	0.12	0.25	The same	″
35.72	21.47	6.86	0.15	0.45	Yellow	″
42.62	21.18	8.18	0.19	0.60	The same	Absent
Pegmatite concentrate:						
17.50	22.10	2.28	0.19	0.11	Light yellow	Present
32.97	21.78	4.26	0.25	0.25	Dark yellow	″
32.62	16.28	5.91	0.44	0.34	The same	Absent
Low-alkali kaolin:						
6.03	24.01	2.05	0.15	0.11	Yellow	Present
2.80	22.39	3.21	0.10	0.19	The same	″
16.00	16.46	4.69	0.39	0.28	Dark yellow	Absent
Alkaline kaolin:						
6.86	22.17	2.10	0.28	0.11	Yellow	Present
7.81	24.13	2.48	0.33	0.13	Dark yellow	″
13.69	16.50	3.88	0.55	0.20	The same	Absent

tion) composition. The content of iron oxides and alkaline metal oxides in such material should correlate with grades PShS 0.20-16, KPShS 0.20-11.5 (GOST 13457–77).

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